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The Reaction of 2, 2'-[l, 2-Ethanediy]bis (thio)] bis-1, 3-dithiolane with Carbonyl Compounds

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The Reaction of 2, 2'-[1, 2-Ethanedithylbis(thio)]bis-1, 3-dithiolane with Carbonyl Compounds

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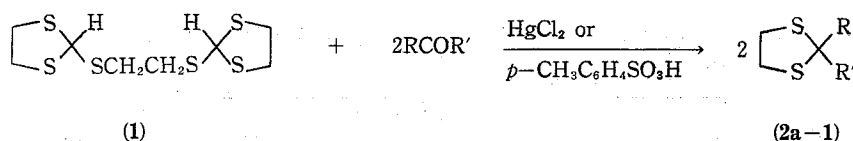
The reaction of 2, 2'-[1, 2-ethanedithylbis(thio)]bis-1, 3-dithiolane with aldehydes or ketones in the presence of either HgCl_2 or *p*-toluenesulfonic acid to form the corresponding 2-substituted or 2, 2-disubstituted 1, 3-dithiolanes was investigated. When some β -keto esters were used as the carbonyl compound, both the corresponding β -keto ester ethylene thioacetals and 1, 3-dithiolan-2-ylated β -keto esters were obtained.

KEY WORDS: Reaction of 2, 2'-[1, 2-ethanedithylbis(thio)]bis-1, 3-dithiolane/ Reaction of aldehydes/ Reaction of ketones/ Reaction of β -keto esters/

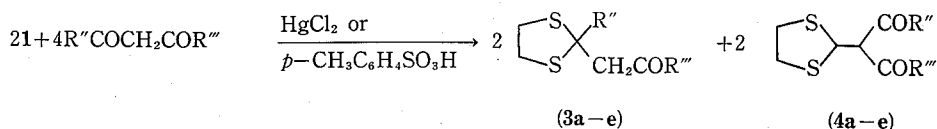
Although 2, 2'-[1, 2-ethanedithylbis(thio)]bis-1, 3-dithiolane (**1**) is easily available by condensation of 1, 2-ethanedithiol with either triethyl orthoformate¹⁾ plus an acid catalyst or formic acid,²⁾ there has not been any information concerning the synthetic utility of this compound. Of the so-called cyclic trithioorthoformates so far reported in the literature, none is known about their reaction excepting the nucleophilic reaction of the lithiated compounds.³⁾ We have recently found the formation of a dianion from **1** and its alkylation with various alkyl halides to afford 1, 2-ethanebis(alkyl trithiocarbonates) and/or dialkyl trithiocarbonates.⁴⁾ We have now observed that **1** also reacts with a variety of carbonyl compounds such as aldehydes, ketones, and β -keto esters in the presence of either HgCl_2 or *p*-toluenesulfonic acid. In the cases of the reaction with aldehydes or ketones, the corresponding 2-substituted or 2, 2-disubstituted 1, 3-dithiolanes (**2**) were obtained in moderately good yields. When the reaction was examined on some β -keto esters under almost similar conditions, the main products were β -keto ester ethylene thioacetals (**3**) and 1, 3-dithiolan-2-ylated β -keto esters (**4**), both of which were already synthesized by us in the reaction of β -keto esters with 2-ethoxy-1, 3-dithiolane.⁵⁾

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Reaction of 2, 2'-[1, 2-Ethanedithiolbis(thio)]bis-1, 3-dithiolane



- (a) $\text{R} = p\text{-ClC}_6\text{H}_4$, $\text{R}' = \text{H}$ (g) $\text{R} = \text{C}_6\text{H}_5\text{CH}=\text{CH}$, $\text{R}' = \text{H}$
 (b) $\text{R} = \text{C}_6\text{H}_5$, $\text{R}' = \text{H}$ (h) $\text{R} = m\text{-CH}_3\text{C}_6\text{H}_4$, $\text{R}' = \text{H}$
 (c) $\text{R} = p\text{-CH}_3\text{C}_6\text{H}_4$, $\text{R}' = \text{H}$ (i) $\text{R} = m\text{-CH}_3\text{OC}_6\text{H}_4$, $\text{R}' = \text{H}$
 (d) $\text{R} = \text{CH}_3(\text{CH}_2)_2$, $\text{R}' = \text{H}$ (j) $\text{R} = m\text{-BrC}_6\text{H}_4$, $\text{R}' = \text{H}$
 (e) $\text{R} = p\text{-NO}_2\text{C}_6\text{H}_4$, $\text{R}' = \text{H}$ (k) $\text{R} = \text{R}' = \text{CH}_3$
 (f) $\text{R} = p\text{-CH}_3\text{OC}_6\text{H}_4$, $\text{R}' = \text{H}$ (l) $\text{R} = \text{R}' = (\text{CH}_2)_5$



- (a) $\text{R}'' = \text{CH}_3$, $\text{R}''' = \text{OC}_2\text{H}_5$ (d) $\text{R}'' = \text{CH}_3$, $\text{R}''' = \text{OC}_3\text{H}_7$
 (b) $\text{R}'' = \text{CH}_3$, $\text{R}''' = \text{OCH}_3$ (e) $\text{R}'' = \text{C}_6\text{H}_5$, $\text{R}''' = \text{OC}_2\text{H}_5$
 (c) $\text{R}'' = \text{R}''' = \text{CH}_3$

Table I. Formation of 2-Substituted and 2, 2-Disubstituted 1, 3-Dithiolanes (2)

R	R'	Eluent used for chromatography	Product ^{a)}	Yield ^{b)} (%) with		Mp (°C) (recryst. from) or bp (°C/torr)
				HgCl ₂	p-CH ₃ C ₆ H ₄ SO ₃ H	
p-ClC ₆ H ₄	H	CH ₂ Cl ₂ /C ₆ H ₁₄ (1:5)	2a	73	84	59-61 (C ₂ H ₅ OH) (lit, ⁸⁾ 62°C)
C ₆ H ₅	H	CH ₂ Cl ₂ /C ₆ H ₁₄ (1:4)	2b	86	83	134-138/3.5 (lit, ⁹⁾ mp 29°C)
p-CH ₃ C ₆ H ₄	H	CH ₂ Cl ₂ /C ₆ H ₁₄ (1:4)	2c	71	78	150-153/4 (lit, ⁸⁾ 198°C/24 torr)
CH ₃ (CH ₂) ₂	H	— ^{c)}	2d	54	68	63-65/3
p-NO ₂ C ₆ H ₄	H	CH ₂ Cl ₂ /C ₆ H ₁₄ (1:2)	2e	61		77-78 (C ₂ H ₅ OH)
p-CH ₃ OC ₆ H ₄	H	CH ₂ Cl ₂ /C ₆ H ₁₄ (1:2)	2f	74	78	59-61 (C ₂ H ₅ OH) (lit, ⁹⁾ 64-65°C)
C ₆ H ₅ CH=CH	H	CH ₂ Cl ₂ /C ₆ H ₁₄ (1:4)	2g	90	82	59-60 (C ₂ H ₅ OH)
m-CH ₃ C ₆ H ₄	H	CH ₂ Cl ₂ /C ₆ H ₁₄ (1:4)	2h	76	83	139-140/4
m-CH ₃ OC ₆ H ₄	H	CH ₂ Cl ₂ /C ₆ H ₁₄ (1:4)	2i	77	78	150-155/3
m-BrC ₆ H ₄	H	CH ₂ Cl ₂ /C ₆ H ₁₄ (1:4)	2j	91	79	158-161/3.5
CH ₃	CH ₃	— ^{c)}	2k	50	89	66-67/17 (lit, ⁹⁾ 171°C/760 torr)
-(CH ₂) ₅ -	— ^{c)}		2l	56		136-139/20 (lit, ¹⁰⁾ 114-115°C/6 torr)

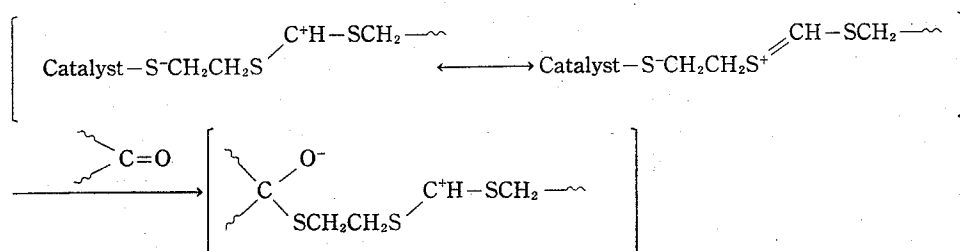
a) The microanalyses were in satisfactory agreement with the calculated values (C ± 0.26 , H $\pm 0.30\%$); spectral data were in accord with the proposed structures. b) Yields are those actually obtained by isolation. c) Isolated by distillation.

Table II. Formation of β -Keto Esters Ethylene Thioacetals (**3**) and 1, 3-Dithiolan-2-ylated β -Keto Esters (**4**)

R''	R'''	Eluent used for chromatography	Product ^{a)} and yield ^{b)} (%) with		Mp(°C) (recryst. from) or bp (°C/torr)
			HgCl ₂	p-CH ₃ C ₆ H ₄ SO ₃ H	
CH ₃	OC ₂ H ₅	C ₂ H ₅ OC ₂ H ₅ /C ₆ H ₁₄ (1:1)	3a (11)	3a (41)	152–157/18 (lit, ¹¹⁾ 86°C/0.1 torr)
			4a (46)	4a (57)	138–140/2 (lit, ⁵⁾ 137.5–139.5°C/2 torr)
CH ₃	OCH ₃	C ₂ H ₅ OC ₂ H ₅ /C ₆ H ₁₄ (1:1)	3b (20)	3b (49)	95–98/2 (lit, ⁵⁾ 94–97°C/2 torr)
			4b (56)	4b (47)	137–138/2.2 (lit, ⁵⁾ 136.5–139.5°C/2 torr)
CH ₃	CH ₃	C ₂ H ₅ OC ₂ H ₅ /C ₆ H ₁₄ (1:1)	3c (13)	3c (35)	142–145/18 (lit, ⁵⁾ 142–145°C/18 torr)
			4c (60)	4c (31)	50–52 (C ₂ H ₅ OH) (lit, ⁵⁾ 50–52.5°C)
CH ₃	OC ₃ H ₇	C ₂ H ₅ OC ₂ H ₅ /C ₆ H ₁₄ (1:1)	3d (14)	3d (37)	112–114/3
			4d (35)	4d (50)	142–146/2.5
C ₆ H ₅	OC ₂ H ₅	C ₂ H ₅ OC ₂ H ₅ /C ₆ H ₁₄ (1:2)	3e (0)	3e (0)	
			4e (42)	4e (58)	44–46 (C ₂ H ₅ OH) (lit, ⁵⁾ 46–49°C)

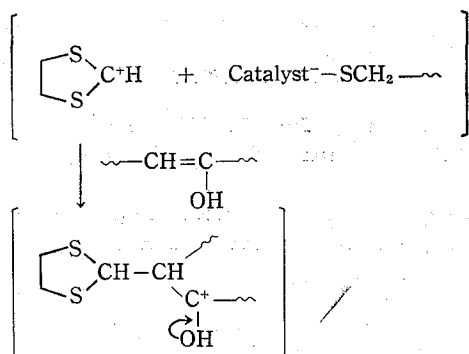
a) All the products gave satisfactory elemental analyses (C \pm 0.29, H \pm 0.20%) and exhibited spectral properties in accordance with the assigned structures. b) Yields are those actually obtained by isolation.

Although the reaction scheme remains unexplored, it is probable that the reaction to form **2** or **3** involves the initial formation of a resonance-stabilized sulfocarbonium ion⁶⁾ as transient intermediate which arises from the C(2)–S bond cleavage of 1, 3-dithiolane rings and the following combination of the ion with a carbonyl carbon.



As is the case of the reaction of 2-ethoxy-1, 3-dithiolane with β -keto esters, the formation of **4** may be explained by a mechanism which involves the transient 1, 3-dithiolan-2-ium ion.⁵⁾

Reaction of 2, 2'-[1, 2-Ethanedithylbis(thio)]bis-1, 3-dithiolane



The most widely used procedure for the synthesis of **2** as masked carbonyl compounds is the one described by Jones and his co-workers.⁷⁾ This method involves the reaction of an aldehyde or ketone with 1, 2-ethanedithiol in the presence of an acid catalyst, usually *p*-toluenesulfonic acid. The present method offers an excellent alternative to the above one, because it is applicable to a wide range of aldehydes or ketones and also the starting material, **1**, is readily available. Supposedly, the reaction conditions of this non-acidic method using HgCl₂ catalyst is mild enough to use on somewhat complex system containing acid-sensitive functional groups. When **1** was allowed to react with ethyl or methyl acetoacetate in the presence of *p*-toluenesulfonic acid catalyst, the total yield of **3** and **4** was 98% or 96%, respectively, suggesting the nearly complete conversion of both **1** and these β -keto esters.

EXPERIMENTAL

Reaction of 2, 2'-[1, 2-Ethanedithylbis(thio)]bis-1, 3-dithiolane (1**) with a Carbonyl Compound in the Presence of HgCl₂.** To a stirred mixture of **1** (2.6 g, 8.6 mmol) and a carbonyl compound (17.2 mmol) in dichloromethane (30 ml) we carefully added HgCl₂ (1.4 g, 5.2 mmol). The mixture was stirred for 24 h at room temperature and then poured into a mixture of aqueous Na₂CO₃ solution and dichloromethane. The insoluble material was removed by filtration and washed repeatedly with dichloromethane, the dichloromethane was combined with a dichloromethane extract of the filtrate. Drying over anhydrous MgSO₄ and removing the solvent gave a crude product, which contains some starting materials. The desired product was isolated by distillation under reduced pressure or by column chromatography on silica gel using the eluent indicated in Tables I and II.

Reaction of 2, 2'-[1, 2-Ethanedithylbis(thio)]bis-1, 3-dithiolane (1**) with a Carbonyl Compound in the Presence of *p*-Toluenesulfonic Acid.** To a mixture of **1** (1.3 g, 4.3 mmol) and a carbonyl compound (8.6 mmol) in dichloromethane (30 ml) we added anhydrous *p*-toluenesulfonic acid (0.75 g, 4.4 mmol). The mixture was refluxed for 6–7 h, and then poured into a large quantity of ether. The ethereal solution was twice washed with 100 ml of aqueous Na₂CO₃ solution followed by 100 ml of cold water. The organic layer was dried (MgSO₄) and evaporated to give a residue. The desired product was isolated in the manner as we have described above.

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